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Assessment of Heavy Metals (As, Cr, Zn) Contamination in Soil from Kawarin Yashe Artisanal Gold Mine, Northwestern Nigeria Using Instrumental Neutron Activation (INAA)

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ABSTRACT

This study was conducted in one of the few locally Gold mines in Katsina State Northwestern Nigeria called Kawarin Yashe Artisanal Gold mines. The concentration of As, Cr and Zn in gold bearing soil in the mines were investigated using instrumental neutron activation analysis (INAA) techniques. Stratified random sampling technique was adopted using soil auger at about 25 - 100 cm to the ground. Experimental results showed that s has a mean concentration of 2.82 ± 0.11 mg/kg, ranging from 0.54 ± 0.14 to 5.11 ± 0.09 mg/kg, Cr has a mean concentration of 46.6 ± 2.0mg/kg ranging from 3.03 to 88.7 ± 105mg/kg and Zn has a mean concentration of 47.96 ± 7.10 mg/kg ranging from 16.30 to 97.2 ± 10mg/kg. The values of As are within the average of 5mg/kg and range 1-50 values, Cr are within the world average values and within the tolerable limit of 100 mg/kg and range of 1-100 mg/kg, respectively. The values of Zn was above the world average of 50 mg/kg. The concentrations obtained in the work are more than the world average values and tolerable limit which implies that the miners and surrounding communities are at risk due to the high concentration of Zn in the area, despite the non-technical nature of the mining activities.

1. INTRODUCTION

Heavy metals are large group of chemical elements that are toxic regardless of their density or atomic mass. These metals occur in the environment of all matrices and have resulted to different exposure levels throughout the history of human existance. Despite the already existing background concentrations of these metals which is vital to human physiology, anthropogenic activities such as mining, transportation, industrial and mechanized agricultural methods were responsible for increasing the concentration of these metals above the acceptable limits in our environment. The United States Agency for Toxic Substances and Disease Registry classified heavy metals Arsenic (As) as mutagens and human carcinogens even at extremely low level exposure (USEPA, 2011) whilst, Zinc (Zn) and Chromium were known to be associated with so

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many non-carcinogenic related consequences, despite the fact that they are essential to life (Ayodele and Muhammed, 2011, Kabala and Singh, 2001). Heavy metals toxicity has proven to be a major threat to human life as there are several health risks associated with them. Though the toxic effects of these metals is more pronounced at a concentration beyond acceptable limits, they do not have any physiological role in the body (Dahiya, 2022). Various studies have shown that the levels of heavy metal contamination in the soil, air, river, and crops from mining affected areas are higher than those in non-mining areas (Bello *et al.*, 2019). Long-term exposure to heavy metals or their compounds can damage the functioning of important body organs and may even cause cancer (Janup, 2003). As cause oxidative stress and renal damage [18]. Intake Zn and Fe in excess of the Recommended Dietary Allowed level was labelled as responsible for manifestations of overt toxicity symptoms. It was established that during DNA repair, even very low quantity of As, Ni and Cd may stop the formation of individual DNA repair protein (Chiroma et al, 2012, Abdullahi et al, 2013). Previous studies in Shanono_Bagwai Northwestern Nigeria have documented significant heavy metal contamination in mining areas, underscoring the necessity for ongoing monitoring and assessment (Bello *et al.*, 2019). Also, heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn may enter the human food chain and result in health problems like the lead poisoning problems in Zamfara State Northwestern Nigeria that kills more than 400 children. (Weekly Trust, 2011).

In this work the concentrations of As, Cr and Zn were determine from Kawarin Yashe Artisanal Gold mine of Katsina State Nigeria using Instrumental Neutron Activation Analysis Techniques.

DESCRIPTION OF THE STUDY AREA

The Kawarin Yashe Village in Kusada Local Government Area of Northern Nigeria. Kawarin Yashe Village, located in Northwestern Nigeria, has a long history of artisanal gold mining, which is a major economic activity for the local population. The Kawarin Yashe village lies in northwestern Nigeria with Coordinates: 12°28′ N 7°59′ E . Kusada Local Government has an area of 390 km^2 and a population of 199,267 at the 2006 census. It falls within a region where rainfall distribution is irregular in time and space and characterized by a prolonged dry season with a short rainy season. The Kawarin Yashe consists predominantly of a gentle undulating plain with an average elevation varying from 540 to 566 m above sea level

The Kawarin Yashe village in Kusada Local Government Area of Northern Nigeria is a potential artisan mining site. This potential mining site lies between latitudes 10°55' and 13°52' N and longitudes 5.00° and 6.00° E in north-western part of Nigeria (Figure 2.1). The Local Government of the study area covered is about 59,570 km^2 and is easily accessible through network of roads. Geomorphologically, this area is generally gentle, with occasionally tabular hills, capped by resistant laterites. Elevation generally decreases towards the northwest around the Kano-Katsina boarder with an average elevation varying from 200 to 250 meters above sea level.

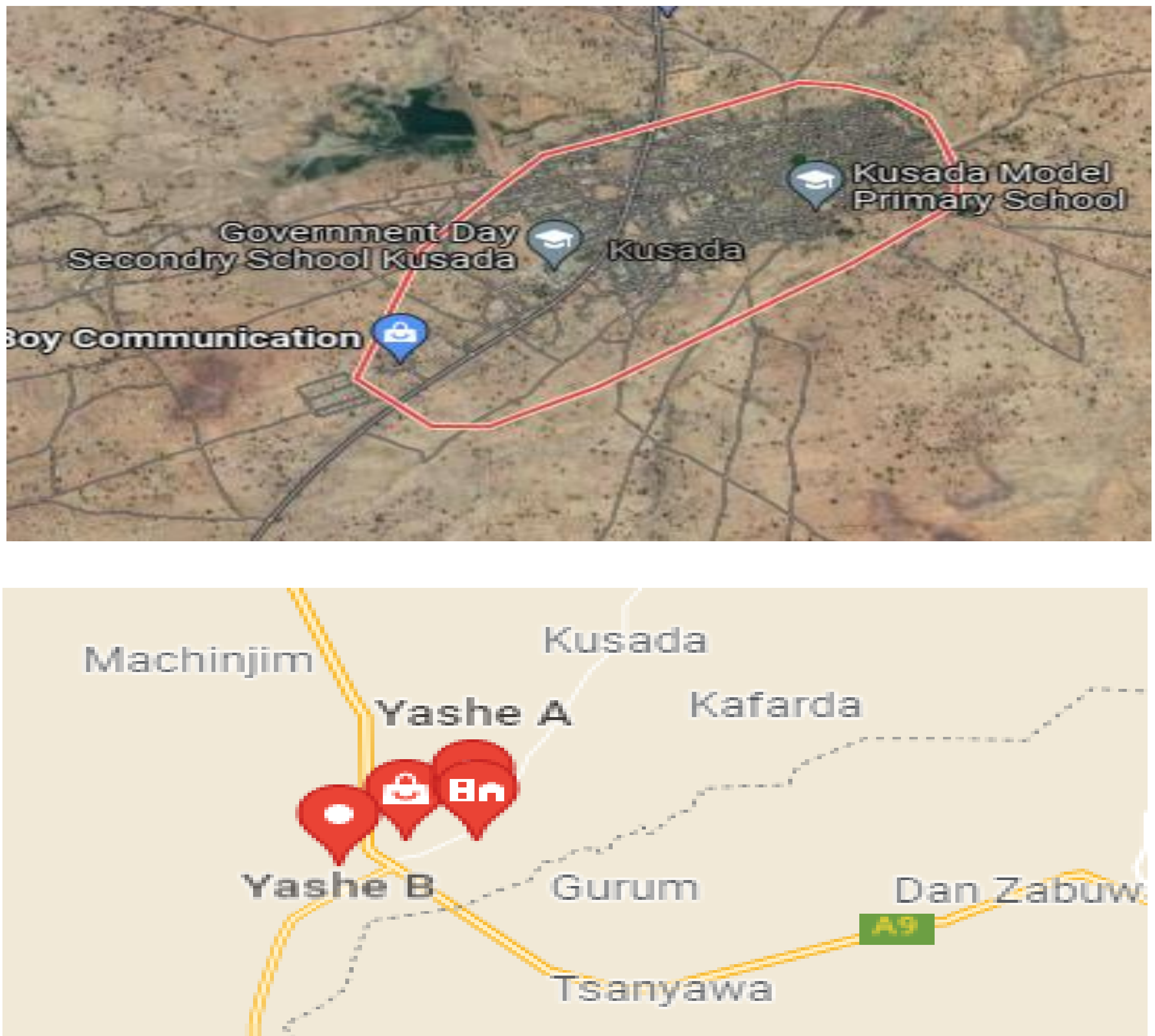

Figure 1: Geographical Map of Nigeria Showing Study Area

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Table 1: Locations and Geological Information for the Positions of Soil Samples

SOIL SAMPLES	ELEVATION(M)	LATITUDE(N)	LONGITUDE(E)	GEOLOGY INFORMATION
Sample 1 SS1	543	12.376122°	7.95701321°	Dry soil sample of Kawarin Yashe Mining Site
Sample 2 SS2	544	12.375603°	7.957945°	Dry soil sample of Kawarin Yashe Mining Site
Sample 3 SS3	545	12.375860°	7.957093°	Dry soil sample of Kawarin Yashe Mining Site
Sample 4 SS4	559	12.377506°	7.944344°	Dry soil sample of Kawarin Yashe Mining Site
Sample 5 SS5	567	12.377608°	7.944808°	Dry soil sample of Kawarin Yashe Mining Site
Sample 6 SS6	566	12.377956°	7.944391°	Dry soil sample of Kawarin Yashe Mining Site

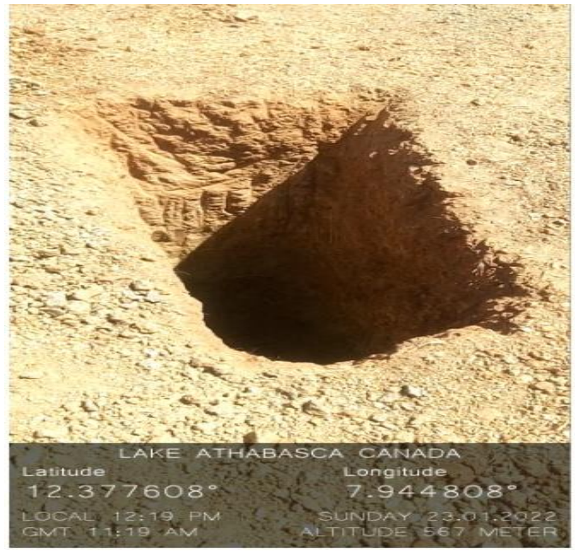


Figure 2**:** Map showing the scope of the study area with simplified Geographical Coordinates of the Sampling Locations and Points.

2. MATERIALS AND METHODS

Six (6) surface soil samples (0-30 cm) in addition to deeper samples to capture a comprehensive contamination profile were collected using soil auger, shovel and digger. The samples were air-dried at room temperature in safe place devoid any mixed-up. The samples were packed in a clean and contamination-free polythene bags and labeled with a marker at the point of collection. The coordinates and elevation of each location was taken using hand held Global Positioning System (Model: GPSMAP 78s). the records were also taken immediately in the record book. The samples were transported to the laboratory for analysis at the Nuclear Science Section, Centre for Energy Research and Training (CERT) of Ahmadu Bello University, Zaria.

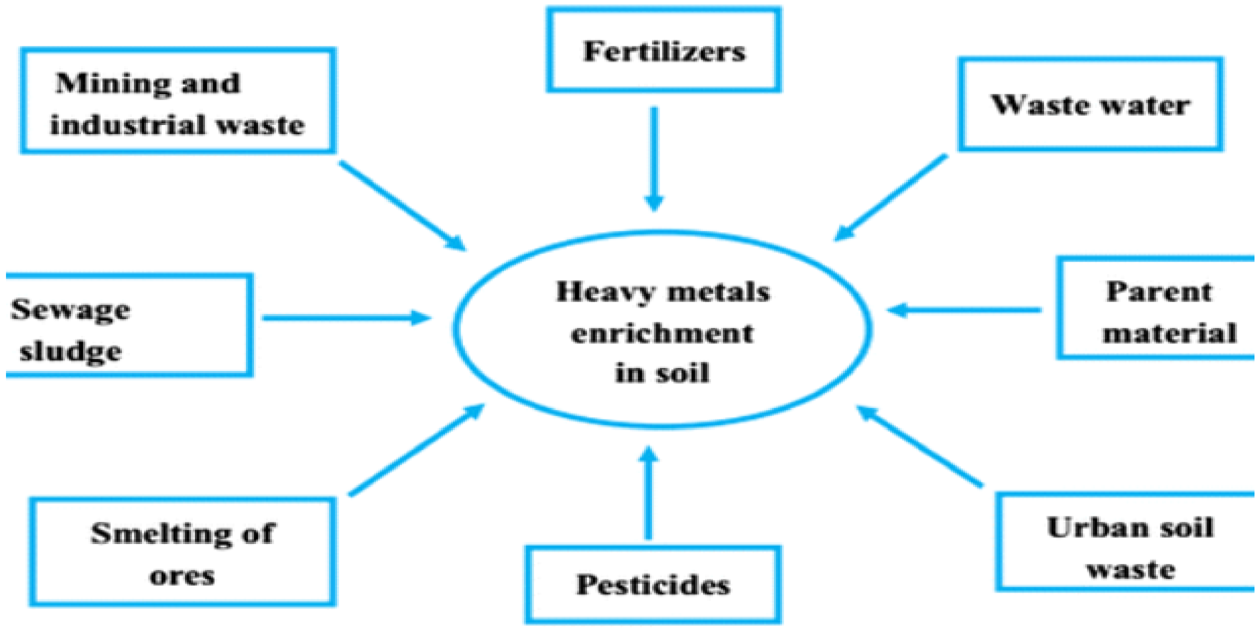
At CERT samples were put on a desiccator and ground using mortar and pestle. A total of 6 (six) samples were prepared. Elemental analysis of the prepared samples was carried out using Instrumental Neutron Activation Analysis (INAA) Technique. INAA is a highly sensitive and accurate method for detecting trace elements in environmental samples, making it ideal for assessing heavy metal contamination in soils. Results of the analysis were obtained from the machine. For verification and quality control purpose, high grade Certified Reference Materials (CRMs) supplied by International Atomic Agency (IAEA) 452 SCALOP, (IAEA) 336 LINCHE were used as comparator standard monitors in this work NIST 1515 and NIST 1547, they were also prepared following the same procedure.

Neutron activation analysis was performed in three (3) main steps: irradiation, detection, and interpretation of results. The irradiation involved two processes covering short-lived and long-lived nuclides as described by Jonah et al. (2005). A flux of neutrons of 5.0 x 1011 $ncm^{-2}s^{-1}$ were accessed during the irradiation. The samples and standards were inserted into the reactor using rabbit carriers under pneumatic pressure. The samples underwent a 6-hour long irradiation using NIRR-1, which delivered a thermal neutron flux of 5.0 x 1011 $ncm^{-2}s^{-1}$. The whole system is equipped with electronic timers which help in monitoring the exact irradiation and decay times. The samples were then brought to a detection setup that included a fixed sample-to-detector geometry and a high purity germanium (HPGe) detector with a relative efficiency of 10% at 1332.5KeV gamma-ray line. The HPGe detector is coupled to a PC-based multi-channel analyzer (MCA). For short lived elements, the first counting was completed 2-15 minutes, and the second one was completed two hours later. The samples were then allowed to decay further for the analysis of the long-life elements. Counting after three (3) days is considered as the first long count and was carried in 30 mins. Furthermore, the samples were cooled for another seven (7) days after which they became ready for the second-long count carried in 1 hour.

3. RESULTS AND DISCUSSIONS

The relative INAA technique has been successfully apply to study the contamination of heavy metals in six (6) samples collected from Kawarin Yashe village. Using INAA, a total of three (3) heavy metals: As. Cr and Zn were detected and measured.

According to the present study it can be established from the results obtained that soils around the Kawarin Yashe have been polluted by the studied heavy metals (Cr, As and Zn). It can also be observed that concentration of As and Zn are below detection limit in some soil samples, because the mining activities are not done in a technical way or has not being commence vigorously. Therefore, the factors that contributed the presence of the studied heavy metals could be attributed to the perennial farming activities around the area in which the farmers used various insecticides, herbicides, emissions from individual irrigation water pumps and corrosion in the irrigation pipe networks.



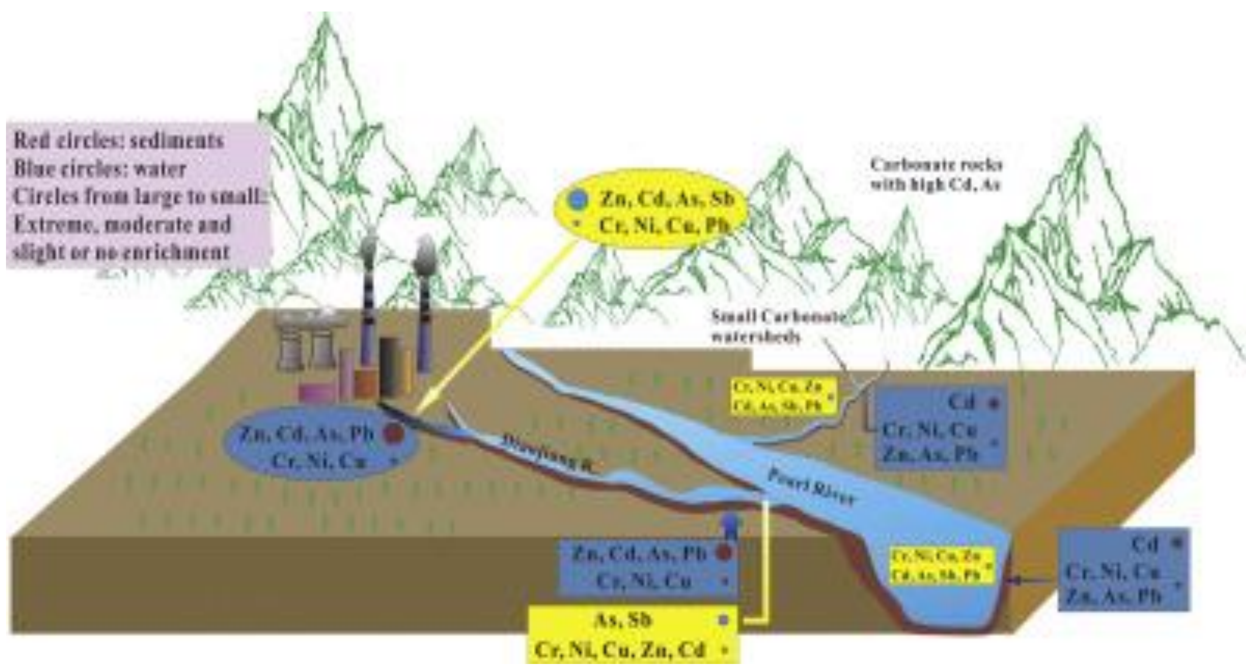


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Table 2: Concentrations of heavy metals with symbols and atomic numbers (in mg/kg)

Element	Symbol	Atomic No	SS 1	SS 2	SS 3	SS 4	SS 5	SS 6
Arsenic	As	33	BDL	5.11±0.09	BDL	BDL	0.54±0.14	BDL
Chromium	Cr	24	BDL	88.71±2.80	BDL	3.03±0.01	38.11±2.30	6.62±2.60
Zinc	Zn	30	16.30± 4.10	97.21±9.50	34.01±6.60	BDL	58.12±6.80	34.21±8.60

Table 3: Concentrations of heavy metals in soils investigated by INAA (in mg/kg)

S/N	SAMPLE	Concentration in mm/kg		
		As	**Cr**	**Zn**
1	Soil Sample 1	**BDL**	**BDL**	16.3± 5.3
2	Soil Sample 2	5.11 ± 0.09	88.7 ± 2.8	97.2 ± 10.5
3	Soil Sample 3	**BDL**	**BDL**	34.1 ± 6.6
4	Soil Sample 4	**BDL**	3.03± 1.7	BDL
5	Soil Sample 5	0.54 ± 0.14	38.1 ± 2.3	58.1 ± 6.8
6	Soil Sample 6	**BDL**	6.6 ± 2.6	34.2 ± 8.6
	Mean	**5.11±0.23**	**136.43±9.2**	**239.8±36.8**

Arsenic (As) was the least accumulated heavy metal in the samples of the present study. Its concentration was observed only in two samples while it was BDL in the remaining samples. Arsenic concentration detected concentrations were of the range (0.54±0.14 to 5.11±0.09 mg/kg). Highest concentration was recorded in SM 2 while the lowest was recorded in SM 5. Arsenic is toxic to humans and can affect people of any age or health status. The maximum permissible limit of 2mg/kg set by WHO (Sandia Corporation, 2000). We must state here that As is seriously toxic when it is greater or equal to 5mg/kg. Arsenic is regarded as human carcinogen from extremely low levels of exposure, having no possible beneficial metabolic functions for humans (NAS/NRC, 1999). Its low-level exposure cause nausea and vomiting decreases the production of RBCs and WBCs, abdominal pain and its long-term exposure causes darkening of skin and appearance of small corns on palm soles. Other effects include abnormal ECG, anorexia, fever, fluid loss, goitre, hair loss, headache, herpes, impaired healing, jaundice, keratosis, kidney and liver damage, muscle spasms, pallor, peripheral neuritis, sore throat, weakness and interferes with the uptake of folic acid (NAS/NRC, 1999).

Chromium (Cr) concentration was only observed in three samples while the remaining samples were at BDL. The detected concentrations are of the range (3.03 to 88.7±2.8 mg/kg), with the highest concentration in SM 2 and SM 5 recorded the lowest**.** None of the samples exceeded permissible limit of Chromium recommended by WHO, though within the world background report (7 – 221 mg/kg), while US permissible limit of 20 to 85mg/kg (Sandia Corporation, 2000). Chromium is a naturally occurring element found in soil, rocks, and plants. Chromium (VI) compounds are toxic and known human carcinogens, whereas chromium (III) is an essential element. Breathing high levels can cause irritation to the lining of the nose; nose ulcers; running nose; and breathing problems, such as asthma, cough, shortness of breath, or wheezing. Long term exposure can cause damage to liver, kidney, circulatory and nerve disorders, as well as skin irritation (Kabata & Pendias, 1993).

Zinc (Zn) recorded concentrations of the range (16.3 to 97.2±10.5 mg/kg) in samples of the studied soil for INAA. The highest concentration was observed in SM 2. while the lowest concentration was noticed in SM 1. Zn is an essential trace metal for both animals and humans, but in excess amount, it may induce toxicity characterized by symptoms of irritability muscular stiffness and pain. The maximum guideline for Zn stipulated by WHO/FAO (1994) is 40 mg/kg. This shows that Zn concentration in SM 2 & SM 4 exceeded the maximum guideline set by WHO/FAO.

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4. **Conclusion**

Neutron Activation Analysis of some soil samples from selected locations of Kawarin Yashe Village of Kusada Local Government Area of Katsina State have been carried out. Some heavy metals such as: arsenic, chromium and zinc were discovered on the mining environment at reasonable levels. This could be attributed to the ongoing uncontrolled mining activities in the area. Therefore, failure to control the exposure will result in severe complications in the future because of the adverse effects imposed by heavy metals. Occupational exposure to heavy metals can be decreased by engineering solutions. Monitoring the exposure and probable intervention for reducing additional exposure to heavy metals in the environment and in humans can become a momentous step towards prevention. National as well as international co-operation is vital for framing appropriate tactics to prevent heavy metal toxicity. Based on the outcome of this study, it is concluded that, prolong mining in the area is not considered safe and therefore, it is recommended that, crucial measures should be taken to reduce the level of contamination of these elements and to ensure proper monitoring for the safety of populace.

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